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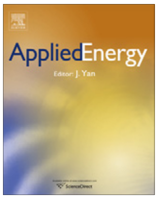

An evaluation on improvement of pulverized biomass property for solid fuel through torrefaction

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ABSTRACT

The improvement on physical and chemical properties of pulverized biomass from torrefaction is investigated to evaluate the potential of biomass as solid fuel used in boilers and blast furnaces. Three biomasses of bamboo, banyan and willow are considered. The results indicate that when the torrefaction temperature is relatively low such as 230 and 260 °C, the weight loss of biomass depends significantly on the temperature, as a result of consumptions of hemicellulose and cellulose. However, once the torrefaction temperature is as high as 290 °C, the weight losses of various biomass materials tend to become uniform. The decreased O/C ratio in biomass from torrefaction can be explained by intensified lignin content in that the O/C ratio in lignin is low compared to that in hemicellulose and cellulose. Furthermore, the enriched element C in torrefied biomass results in an increase in the calorific value of the torrefied materials. However, the enlarged higher heating value (HHV) of biomass from torrefaction cannot keep up with the weight loss; this leads to the decrease in total energy of biomass as the torrefaction temperature rises. The conducted correlation in predicting the HHV of raw biomass can also be utilized for torrefied biomass. The raw pulverized biomasses are characterized by agglomeration in the regime of smaller particle size. Once the biomasses undergo torrefaction, the dispersion of powder is improved, thereby facilitating the injection of biomass powder. This enhances the applications of pulverized biomass in boilers and blast furnaces.

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1. Introduction

Biomass is an important source of energy in the world. For example, according to the statistics of International Energy Agency (IEA), it is known that biomass account for around 10% of primary energy demand worldwide in 2005 [1]. Biomass can be converted into gas products by gasification; it can also be transformed into liquid fuels, such as biooil, biodiesel and bioethanol, via pyrolysis, transesterification as well as fermentation and saccharification [2–5]. Aside from transformation into gas and liquid products, biomass can also be combusted directly or co-fired with coal in boilers or blast furnaces for heat and power [6–8]. While biomass is consumed as a fuel or for energy, how to utilize it with high efficiency is of the utmost importance. However, different biomasses are characterized by their diversity in physical and chemical properties [9]. This makes difficulties and challenges encountered when handling raw biomass for fuel or energy. As far as pulverized biomass is concerned, it has been extensively co-fired with coal in utility boilers for power generation [10]. Generally speaking, biomass is characterized by higher amount of volatile matter, less ash, lower density and lower heating value [11]. By virtue of higher volatile matter, this results in less char to be produced and burned in combustors. Moreover, the reactivity of biomass is higher than that of coal, rendering that the ignition and burning time of biomass are quite different from those of coal [12].

To use bioenergy efficiently, a variety of pretreating methods of biomass have been developed. One of the methods is torrefaction [13–17]. Torrefaction is a thermal pretreatment process where raw biomass is heated in a non-oxidizing atmosphere with the temperatures of 200–300 °C [18,19]. To achieve thermal degradation but avoid oxidation of biomass, nitrogen is usually used to provide an inert environment. It is well known that the principal and basic constituents in biomass are hemicellulose, cellulose and lignin [20]. Apart from these constituents, hygroscopic by nature, fresh biomass also contains a large amount of moisture [18]. It has been reported that the thermal degradation temperatures of hemicellulose, cellulose and lignin are in the ranges of 150–350, 275–350 and 250–500 °C, respectively [21,22]. Accordingly, when biomass is torrefied, not only moisture is expelled but also parts of the basic constituents are degraded due to high temperature environments. In general, torrefaction consumes hemicellulose

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markedly, whereas the degradation extents of cellulose and lignin depend strongly on the adopted torrefaction temperature [14].

Because there is no external oxygen supplied in the course of torrefaction, partial element oxygen contained in raw biomass is consumed for the reactions of biomass. For this reason, it has been reported that the O/C ratio of torrefied biomass is always lower than the counterpart of the untreated biomass [23]. While light volatiles contained in biomass are emitted as a result of heat being conducted into the material, the carbonization reaction in biomass also proceeds. As a consequence, another important characteristic accompanied by torrefaction is that the heating value of torrefied biomass is always higher than its parent biomass [24]. In addition, by virtue of the variation in internal structure of biomass, it has also been highlighted that torrefied biomass is characterized by hydrophobic behavior and improved grindability [25,26]. Accordingly, after experiencing torrefaction the properties of biomass are more close to those of coal. It is thus anticipated that it is more feasible to co-fire blends of biomass and coal.

Reviewing past literature concerning torrefaction indicates that most of the studies were focused on the experiments of biomass chips or blocks [13,25,27,28]. In contrast, relatively little work has been performed on the impact of torrefaction upon pulverized biomass. When biomass is pulverized into powder, they can be injected into a boiler as a fuel for generating heat and power or blown into a gasifier as a feedstock to produce syngas. The powder can also be blended with pulverized coal and injected into a blast furnace for the purpose of producing hot metal [29,30]. On account of the multiple applications of pulverized biomass, this study is intended to investigate the property variation of pulverized biomass undergoing torrefaction. An evaluation on the applications of pulverized biomass with torrefaction for fuels will also be carried out.

2. Experimental

2.1. Reaction system

A schematic of the experimental system and procedure is shown in Fig. 1. The system was made up of a nitrogen steel cylinder, a rotameter, a reactor and a product gas treatment unit. The steel cylinder was used to supply nitrogen for providing a non-oxidizing or torrefaction environment. The volumetric flow rate of nitrogen was controlled by the rotameter. The reactor comprised a glass reaction tube and a heater (or electrical furnace). The tested samples were placed in the tube for torrefaction and the heater was used to elevate and sustain the reaction temperature. The reaction temperature was controlled by a proportional integral derivative (PID) temperature controller, whereas the power of the heater was controlled by a solid state relay (SSR) power controller. In the product gas treatment unit, a conical flask was employed to remove tar and clean exhaust gas.

2.2. Experimental procedure

Before experiments were carried out, raw biomasses were ground into powders by a shedder. Then, the powders were sieved by a vibrating screen. The particle sizes of the tested samples were controlled between 100 and 200 mesh (i.e. 75–150 μm). The sieved biomasses were dried in an oven with the temperature of 105 °C for 24 h to provide a basis for experiments. In each run, the pulverized powder with the total mass of 9.5 g (±5%) was placed in the reaction tube. After the samples were in the tube, they were torrefied for 1 h. While the samples were torrefied, the flow rate of nitrogen was fixed at 100 mL min^{-1} (25 °C) and it was continuously blown into the reaction tube to keep the reaction tube in an inert environment and to remove volatile products from the thermal degradation of biomass. Soon after the gas mixture left from the reactor, they were cooled and washed in the conical flask. Prior to performing experiments, the reaction system was leak tested using nitrogen to ensure the measurement quality. The experiment under any given condition was usually carried out more than twice. The results were fairly uniform between each run and the relative error was less than 5%.

2.3. Material analysis

In this study, the raw biomasses and torrefied materials were extensively analyzed. The measurements of the raw and torrefied materials include proximate, elemental (ultimate), fiber, calorific,

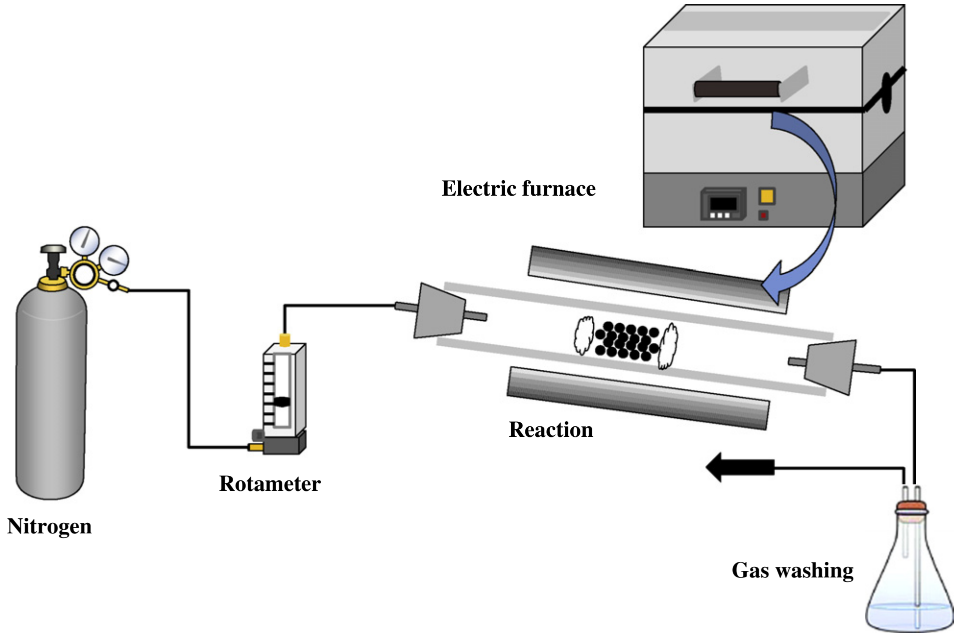

Fig. 1. A schematic of biomass torrefaction system.

thermogravimetric and particle size analyses. The proximate analysis was performed in accordance with the standard procedure of American Society for Testing and Materials. The elemental analysis was carried out using an elemental analyzer (Elementar Vario EL III). In regard to the fiber analysis, hemicellulose, cellulose and lignin were analyzed following the method adopted in a previous study [31]. The higher heating values (HHVs) of the samples were measured by a bomb calorimeter (IKA C2000 Basic). The thermogravimetric analysis (TGA) was performed by use of a thermogravimetry (PerkinElmer Diamond TG/DTA). The non-isothermal thermogravimetric analysis with the heating rate of 20 °C min^{-1} where the temperature ranged from 25 to 800 °C was executed and the flow rate of N_2 was 100 cc min^{-1}. Considering particle size distribution, it was examined by a laser diffraction analyzer (HORIBA LA 950V2). The raw samples and torrefied materials were also observed through a scanning electron microscope (SEM, FEI Quanta 400F).

3. Results and discussion

Attention of this study is focused on the impact of torrefaction upon the physical and chemical properties of pulverized biomass. Three different biomasses are taken into account; they are bamboo, banyan and willow. The basic properties of the materials such as proximate, fiber, elemental and calorific analyses are listed in Table 1. On the other hand, to extensively explore the influence of torrefaction temperature on the biomasses, three torrefaction temperatures of 230, 260 and 290 °C were considered. In a previous study [14], it has been outlined that one hour heating was an appropriate procedure for biomass torrefaction. Because of this, the aforementioned period serves as the basis of investigation.

3.1. Variations of weight and elements of biomass

The impact of torrefaction temperature on biomass weight is first demonstrated in Fig. 2 where the weight loss has been nondimensionalized in terms of the original biomass weight. As can been seen in the figure, bamboo is the most active biomass to torrefaction, regardless of what the torrefaction temperature is. Specifically, over 50% of weight is lost from torrefaction even though the temperature is as low as 230 °C. Table 1 indicates that the content of hemicellulose in bamboo is the highest (i.e. 28%) among the three biomasses. It has been known that the thermal degradation of hemicellulose is relatively violent compared to cellulose and lignin in a high temperature environment [14]. This is the reason that the impact of torrefaction in bamboo is pronounced. In contrast, the content of lignin in banyan is relatively abundant and lignin has a higher resistance to thermal degradation. This results in that the weight loss of banyan is less drastic at the torrefaction temperatures of 230 and 260 °C. Considering the three materials in the torrefaction temperature of 290 °C, it is worthy of note that the weight loss is close to 60% which is almost independent of the tested materials. This reflects that the properties of the torrefied materials tend to become uniform. However, only around 40% of mass is retained from the severe torrefaction at 290 °C.

Table 1
Proximate, fiber, elemental and calorific analyses of raw bamboo, banyan and willow.

Raw material	Bamboo	Banyan	Willow
Proximate analysis (wt.%)			
Moisture	2.99	3.29	3.47
Volatile matter (VM)	73.56	77.57	80.29
Fixed carbon (FC)	19.94	18.03	15.57
Ash	3.51	1.11	0.67
Fiber analysis (wt.%)			
Hemicellulose	28.03	12.19	21.31
Cellulose	55.01	57.07	63.69
Lignin	16.96	30.74	15.00
Elemental analysis (wt.%, db[a])			
C	43.84	46.20	45.80
H	6.05	6.08	6.24
N	0.07	0.08	0.09
O	46.53	46.53	47.20
HHV (MJ kg^{-1})	18.70	20.29	19.61

[a] Dry basis.

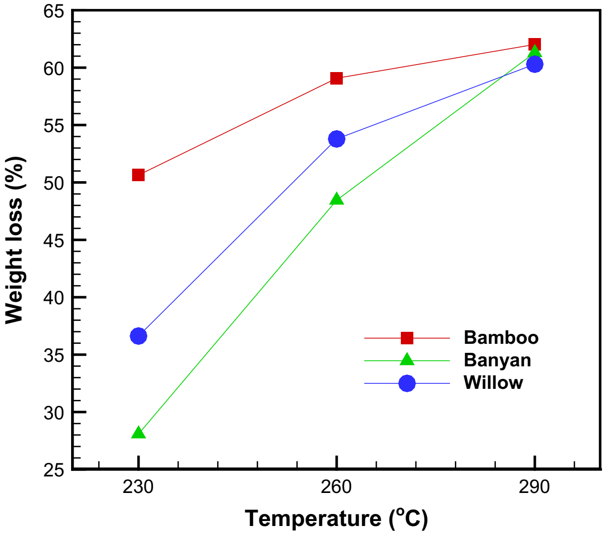

Fig. 2. Weight loss distributions of three tested biomasses with respect to torrefaction temperature.

The measured weight percentages of elements C, H, N and O as well as HHV of the raw and torrefied biomasses are listed in Table 2 for comparison. It is evident that the weight percentage of C increases significantly with increasing torrefaction temperature. On the contrary, the weight percentage of O has a trend to decrease with temperature. When the value of O/C ratio is examined, as shown in Fig. 3, one can find that the ratio decays from 1–1.10 to 0.30–0.35. In lignocelluloses, hemicellulose is a polymer with a basic structure of $(C_5H_8O_4)_m$ [32], whereas the basic structure of cellulose can be denoted by $(C_6H_{10}O_5)_m$ where m is degree of polymerization [33]. It follows that corresponding to hemicellulose and cellulose the O/C ratios are 0.8 and 0.83, respectively. Meanwhile, the basic structure of lignin is represented by $[C_9H_{10}O_3\cdot(OCH_3)_{0.9\text{-}1.7}]_m$ [32], implying that the O/C ratio in lignin is in the range of 0.43–0.52. On account of pyrolytic nature of torrefaction, partial O contained in biomass will be consumed for thermal degradation. In addition, the consumption of hemicellulose and cellulose from torrefaction is more pronounced than that of lignin, especially in hemicellulose. This results in that the O/C ratio in biomass undergoing torrefaction is abated.

3.2. Thermogravimetric analysis (TGA)

To proceed farther into an analysis of the impact of torrefaction upon lignocelluloses, the thermogravimetric analyses (TGA) and derivative thermogravimetric (DTG) analyses of the three tested samples in the environment of N_2 are plotted in Figs. 4–6. It can be found that the thermal decomposition of raw bamboo mainly occurs within the temperatures of 200–350 °C (Fig. 4a). In examining the DTG curve, the thermal degradations of hemicellulose and cellulose can be identified (Fig. 4b). With the torrefaction temperature of 230 °C, Fig. 4b also depicts that large portions of hemicel-

Table 2
Elemental and gross calorific analyses of raw and torrefied biomass.

Material	Temperature (°C)	Elemental analysis (wt.%, db)				Ash (wt.%)	HHV (MJ kg^{-1})	Enhancement in HHV (-)
		C	H	N	O			
Bamboo								
	Raw	43.84	6.05	0.07	46.53	3.51	17.55	1
	230	56.68	6.18	0.17	32.42	4.55	23.62	1.346
	260	62.26	6.29	0.13	24.64	6.68	26.46	1.508
	290	64.58	6.56	0.16	19.31	9.39	28.08	1.600
Banyan								
	Raw	46.20	6.08	0.08	46.53	1.11	18.46	1
	230	53.55	6.84	0.15	37.08	2.38	22.87	1.239
	260	60.73	6.46	0.18	28.52	4.11	25.77	1.396
	290	66.21	6.22	0.15	22.57	4.85	28.00	1.517
Willow								
	Raw	45.80	6.24	0.09	47.20	0.67	18.45	1
	230	56.59	6.41	0.14	34.21	2.65	23.71	1.286
	260	65.16	7.10	0.23	24.33	3.18	28.53	1.547
	290	67.55	7.06	0.22	20.92	4.25	29.64	1.607

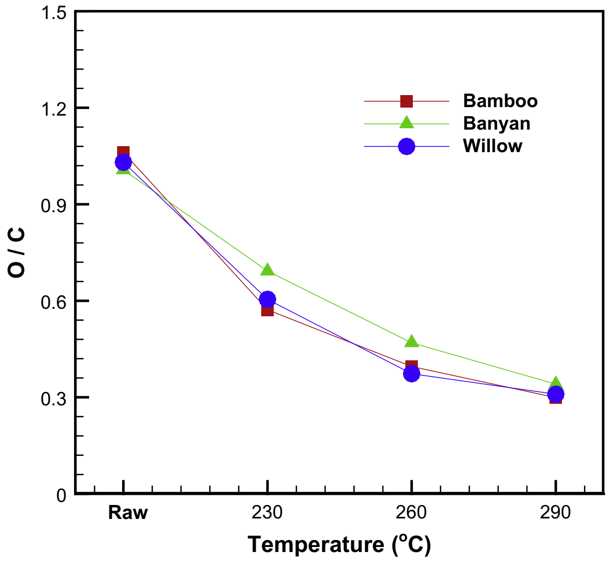

Fig. 3. Distributions of O/C ratio of three tested biomasses with respect to torrefaction temperature.

lulose and cellulose disappear, verifying that bamboo is a sensitive biomass to torrefaction. For this reason, once bamboo undergoes torrefaction, the weight loss distribution in the TGA curve becomes relatively insensitive (Fig. 4a). Unlike the results exhibited in Fig. 4a, the TGA curves of banyan and willow shown in Figs. 5a and 6 a indicate that increasing torrefaction temperature progressively reduces the thermal degradation of biomass. The DTG curves shown in Figs. 5b and 6b indicate that most of the cellulose contained in banyan and willow are retained when the torrefaction temperature of 230 °C is carried out. It is thus recognized that cellulose in bamboo is relatively active in a high temperature environment. If the torrefaction temperature of 260 °C is executed, it can be found that only cellulose in banyan can be identified (Fig. 5b), revealing that the cellulose in banyan possesses the highest resistance to thermal degradation among the three biomasses. Once the torrefaction temperature is as high as 290 °C, only lignin can be pointed out. This implies, in turn, that large portions of hemicellulose and cellulose are consumed from the specified torrefaction temperature.

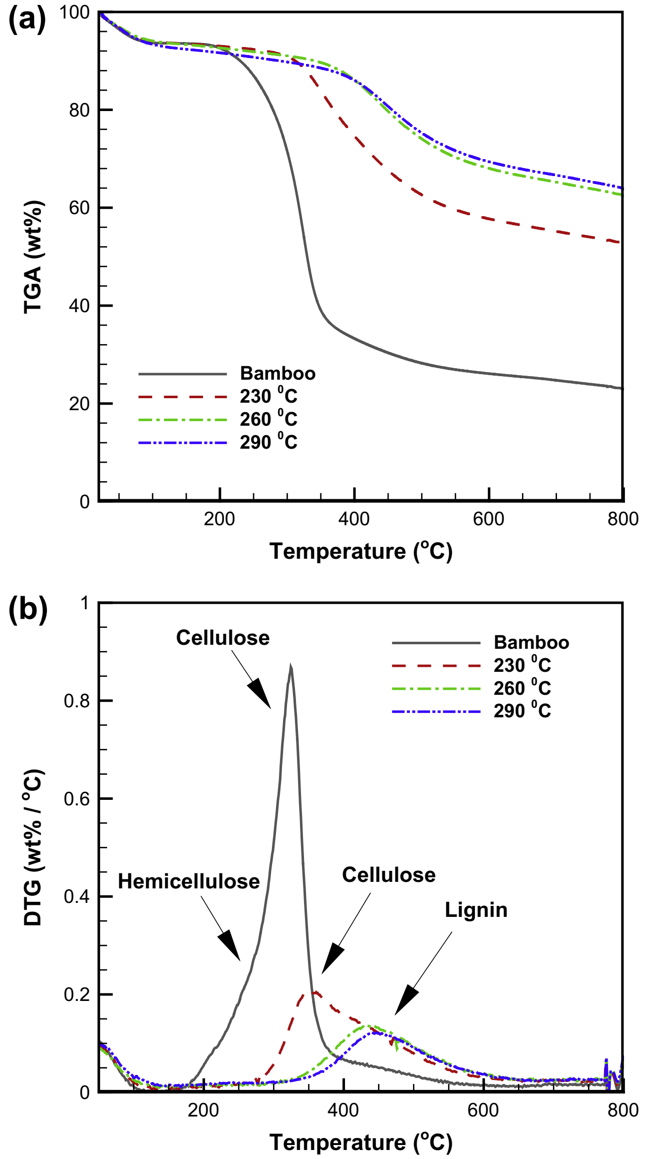

Fig. 4. Distributions of: (a) TGA and (b) DTG of raw bamboo and torrefied bamboo undergoing three different torrefaction temperatures.

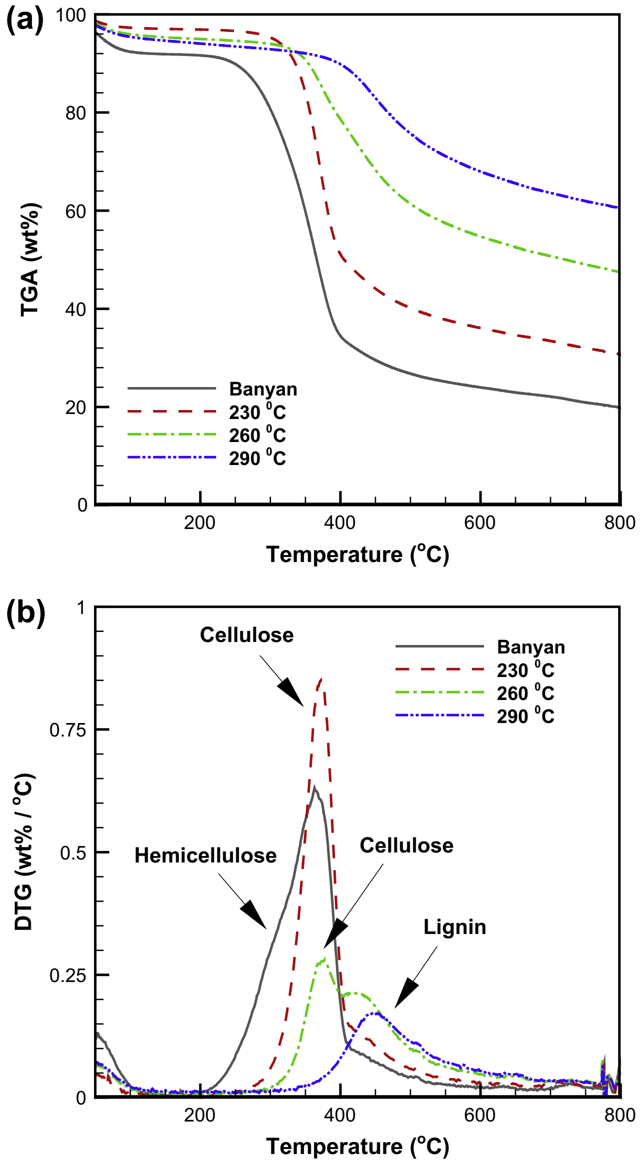

Fig. 5. Distributions of: (a) TGA and (b) DTG of raw banyan and torrefied banyan undergoing three different torrefaction temperatures.

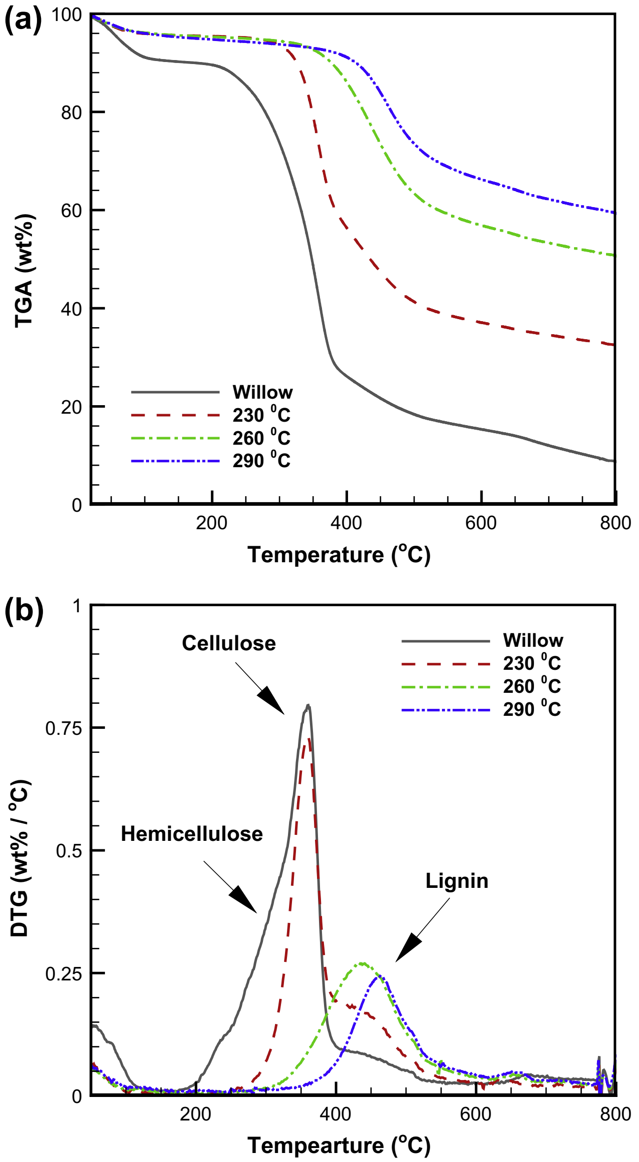

Fig. 6. Distributions of: (a) TGA and (b) DTG of raw willow and torrefied willow undergoing three different torrefaction temperatures.

3.3. Heating value of biomass

When one is concerned with HHV of biomass, it has been known that C plays an exothermic role as a fuel is burned, whereas O plays an endothermic role. As seen in Table 2, the higher the torrefaction temperature, the higher C and the lower O (Table 2). This leads to the increase of HHV of biomass as the torrefaction temperature rises, as shown in Fig. 7a. If the HHV of raw biomass is selected as the basis, Table 2 suggests that the HHV of bamboo, banyan and willow are enlarged by factors of 1.40, 1.32 and 1.46, respectively, at the torrefaction temperature of 290 °C. Despite the enhancement of HHV from torrefaction, it should be addressed that the weight loss of biomass is lessened at the same time. To recognize the total energy contained in biomass affected by torrefaction, the ratio of total energy between raw biomass and torrefied biomass is plotted in Fig. 7b where the total energy is defined as the multiplication of HHV and residual weight of a torrefied sample. It is clear that around 64–82% of total energy is retained in torrefied biomass when the samples are treated at 230 °C; alternatively, with the torrefaction temperature of 290 °C the total energy contained in biomass decays to 51–58%. Obviously, the intensified HHV from torrefaction is insufficient to counteract the weight loss of biomass. As a result, a monotonic decrease in the total energy ratio with increasing torrefaction temperature is exhibited. It is also noted that the decreasing tendency in the total energy ratio of banyan is much more drastic than those of bamboo and willow. This implies, in turn, that that a higher torrefaction temperature has larger influence on the total energy of relatively inactive biomass (e.g. banyan).

Conventionally, HHV of biomass is measured by a bomb calorimeter; it can also be evaluated from the proximate analysis and the elemental analysis [9,34]. However, the correlation in accordance with the elemental analysis and the proximate analysis was established from raw biomass with dry basis. In view of the pronounced variation in weight percentage of element when biomass undergoes torrefaction (Table 2), one of the interests of this study is on the feasibility of HHV predicted from the empirical correlation in terms of elemental and proximate analyses. In the study

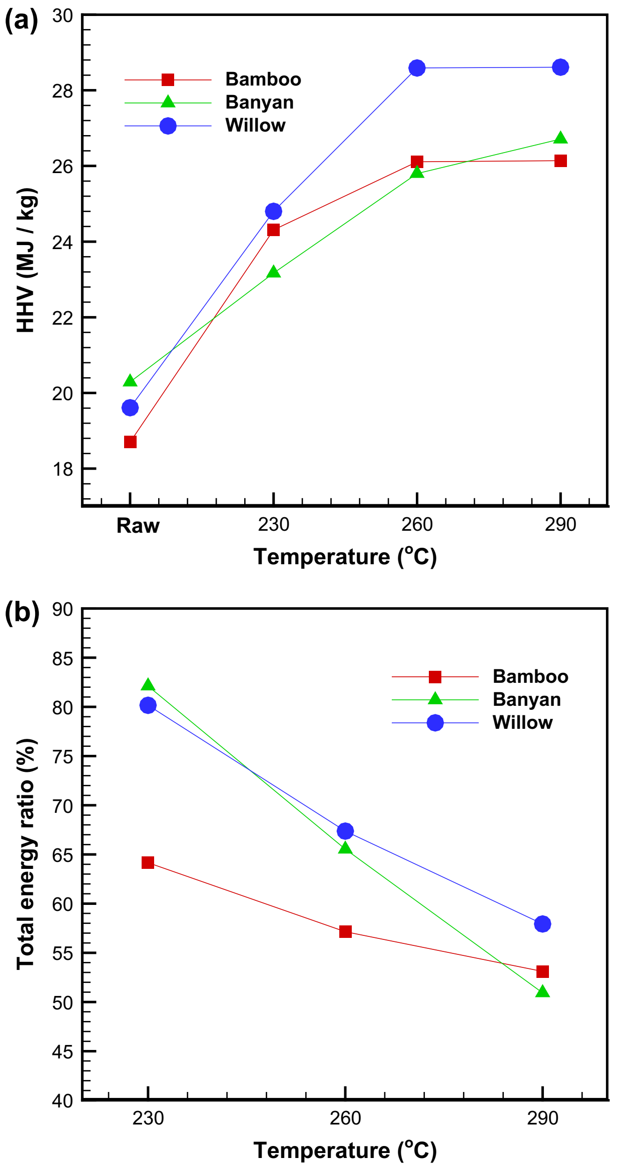

Fig. 7. Distributions of: (a) higher heating value (HHV) and (b) total energy ratio of the three tested biomasses with respect to torrefaction temperature.

of Channiwala and Parikh [34], they have developed an empirical correlation based on elemental and proximate analyses to predict the HHV of raw biomass. The correlation is expressed by

$$\mathrm{HHV}(\mathrm{MJ\ kg^{-1}}) = 0.3491\mathrm{C} + 1.1783\mathrm{H} + 0.1005\mathrm{S} - 0.1034\mathrm{O} - 0.0151\mathrm{N} - 0.0211\mathrm{A} \quad (1)$$

In the above equation, C, H, S, O, N and A represent the weight percentages of carbon, hydrogen, sulfur, oxygen, nitrogen and ash in biomass, respectively. The measured and predicted HHVs of the three raw biomasses and the torrefied materials based on the aforementioned equation are tabulated in Table 3 and compared with each other. In the table, the relative error is defined by

$$\text{Relative error}(\%) = \left|\frac{\mathrm{HHV}_{\mathrm{measurement}} - \mathrm{HHV}_{\mathrm{prediction}}}{\mathrm{HHV}_{\mathrm{measurement}}}\right| \times 100\% \quad (2)$$

Apparently, the relative errors between the measurements and predictions are within 10%, especially for the torrefied biomass where the relative error is below 5.3%. Consequently, it should be pointed out that the empirical correlation also enables us to predict the HHV of torrefied biomass.

Table 3
Comparison of HHV of raw and torrefied biomass between measurement and prediction.

Material	Temperature (°C)	Measurement (MJ kg^{-1})	Prediction (MJ kg^{-1})	Relative error (%)
Bamboo				
	Raw	18.699	17.55	6.16
	230	24.308	23.62	2.84
	260	26.110	26.46	1.32
	290	26.142	28.08	7.40
Banyan				
	Raw	20.289	18.46	9.03
	230	23.169	22.87	1.30
	260	25.798	25.77	0.09
	290	26.708	28.00	4.85
Willow				
	Raw	19.609	18.45	5.93
	230	24.801	23.71	4.39
	260	28.586	28.53	0.21
	290	28.611	29.64	3.61

The above results have clearly indicated that the heating value of biomass undergoing torrefaction can be intensified significantly. Basically, the pelletization of biomass also possesses the same merit. For example, in the study of Wahlund et al. [35], it has been reported that a conventional biomass-based combined heat and power plant with integrated pellet production has great potential for reducing CO_2 and increasing efficiency. In another study [36], it was highlighted that biomass refining into pellets enables transportation over long distances and seasonal storage. It follows that both biomass pelletization and torrefaction can increase the heating value of biomass and improve the efficiency of using biomass as a fuel, thereby reducing the emissions of greenhouse gas.

3.4. Particle size distribution and SEM observation

With attention focused on particle size distribution, Figs. 8 and 9 display the distributions of powder size and volume accumulation of the tested materials, respectively. When bamboo is examined, Figs. 8a and 9a reveal that the effect of torrefaction on particle size distribution is not notable. For raw bamboo particles approximately ranging from 5 to 30 μm, a small extent of agglomeration is observed. After experiencing torrefaction, a more uniform distribution in particle size is obtained, no matter what the torrefaction temperature is. Regarding raw banyan and willow, it is noteworthy that the smaller particles are significantly featured by agglomeration in that the double-peak distributions are observed (Fig. 8b and c). Upon inspection of the proximate analyses of the three raw biomasses (Table 1), it can be found that the values of VM of bamboo, banyan and willow are 73.6, 77.6 and 80.3%, respectively. VM is inherently a mixture of short chain and long chain hydrocarbons as well as aromatic hydrocarbons. Clearly, a higher VM in biomass makes the agglomeration of powder more pronounced. Once banyan and willow undergo torrefaction, it is of interest that the characteristic of agglomeration is eliminated, as a consequence of normal distribution being behaved. This is the reason that the difference of volume accumulation between the raw biomass and the torrefied biomass is intensified when comparing Fig. 9b and c to a. From the viewpoint of biomass applied in boilers and blast furnaces, if biomass powder is characterized by agglomeration, a difficult operation in powder injection will be encountered. In this aspect, it is thus discovered that torrefaction also possesses the merit of diminishing agglomeration of pulverized biomass, thereby improving the operation of powder injection in boilers and blast furnaces.

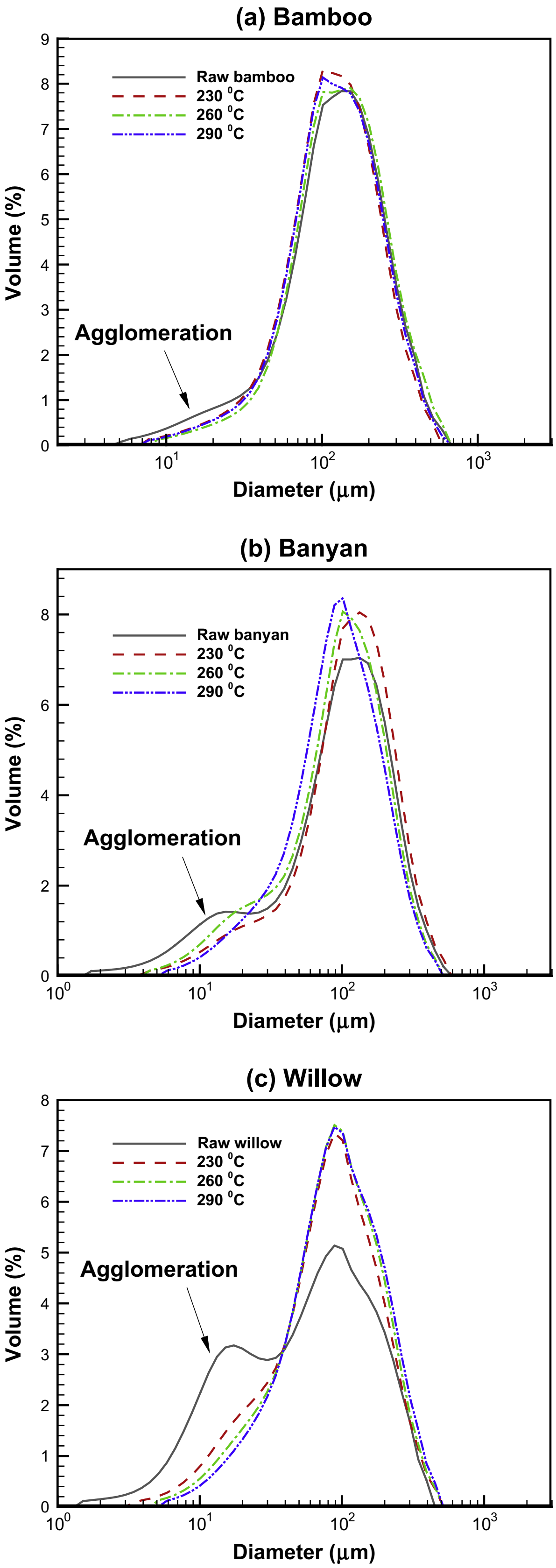

Fig. 8. Particle size distributions of: (a) bamboo (b) banyan and (c) willow before and after undergoing torrefactions.

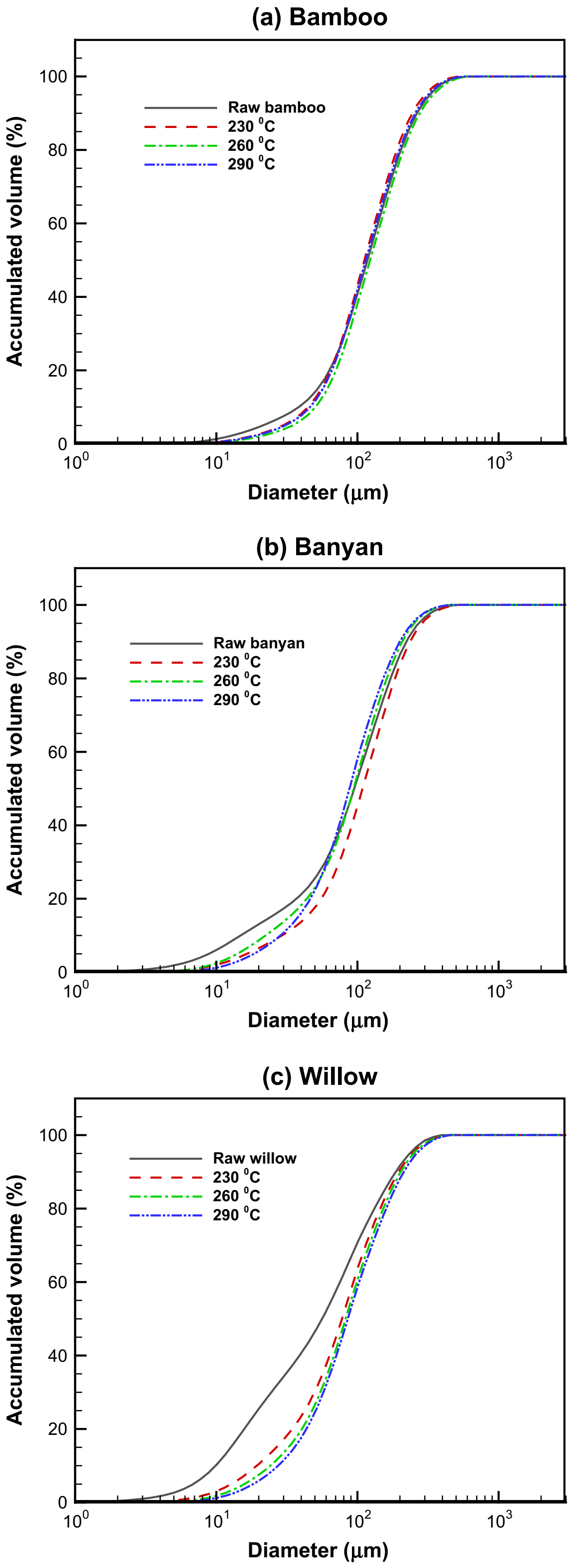

Fig. 9. Accumulated particle size distributions of: (a) bamboo (b) banyan and (c) willow before and after undergoing torrefactions.

To gain a deeper insight into the impact of torrefaction on pulverized biomass, the scanning electron microscope (SEM) images of the three biomasses before and after torrefaction are shown in Fig. 10. The images have been amplified by a factor

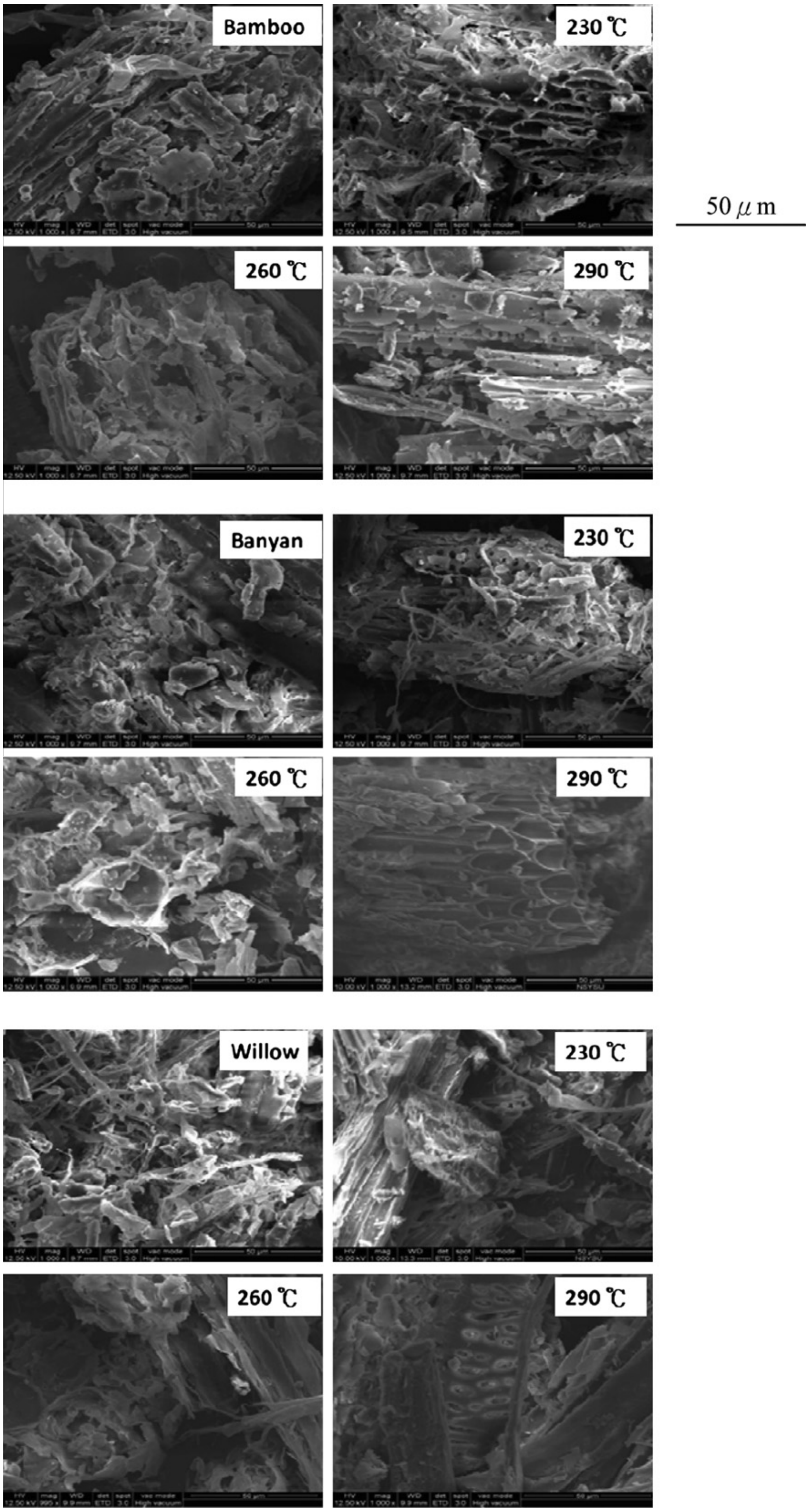

Fig. 10. SEM images of: (a) raw and torrefied bamboo, (b) raw and torrefied banyan and (c) raw and torrefied willow.

of 1000. Regarding the raw biomasses, the microstructure on the surfaces can be clearly observed, especially on the surface of raw willow where some microfibers are seen obviously. Increasing torrefaction temperature enhances the impact of thermal pretreatment on the biomasses and consumes more tiny particles. This results in the curves shown in Fig. 9 being shifted rightwards. While the tiny powder diminishes, the impact of torrefaction on internal structure of biomass is also evidently observed. For example, with the torrefaction temperature of 290 °C, the particle surfaces of bamboo and banyan are filled with tiny holes and characterized by tubular structure, respectively.

4. Conclusions

The effect of torrefactions on the improvement of physical and chemical properties of pulverized biomass has been investigated in this study; particular emphasis is placed upon the applications of pulverized biomass in boilers and blast furnaces. Three biomasses of bamboo, banyan and willow, which are in the mesh numbers of 100 and 200, have been tested. The important concluding remarks are drawn below.

1. When the torrefaction temperature is relatively low, such as 230 or 260 °C, the weight loss of biomass undergoing torrefaction depends strongly on the lignocellulosic nature of biomass. It is found that bamboo and banyan are relatively active and inactive to torrefaction, respectively. However, once the torrefaction temperature is as high as 290 °C, the weight loss tends to become uniform.
2. The decreased O/C ratio in biomass with increasing torrefaction temperature can be partially explained by the consumptions of hemicellulose and cellulose from torrefaction, resulting from higher O contained in these constituents.
3. The gross calorific value (or HHV) of biomass can be intensified up to by a factor of 1.46 from torrefaction. However, the total energy of biomass abates with increasing torrefaction temperature, attributed to the fact that the enlarged HHV is insufficient to counteract the weight loss. Despite pronounced variation in elemental percentage from torrefaction, the conducted correlation in predicting HHV of raw biomass is also applicable for the prediction of HHV of torrefied biomass.
4. The agglomeration phenomenon characterizes the smaller particles of the pulverized biomass. The higher the VM contained in biomass, the more drastic the agglomeration behavior. The thermal pretreatment via torrefaction significantly removes the agglomeration phenomenon. Therefore, the operation of pulverized biomass injection in boilers or blast furnaces can be improved markedly.
5. From the present study, it is known that if biomass is torrefied followed by pelletization, the heating value and efficiency of the processed biomass can be further promoted. The efficiency of the torrefied biomass pellet has been preliminarily evaluated in the study of Uslu et al. [37]. The combination of torrefaction and pelletization deserves further investigation in the future.

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